J Supercond Nov Magn (2009) 22: 119–121
DOI 10.1007/s10948-008-0405-1

ORIGINAL PAPER

Effect of Vacuum and O_2 Annealing Treatments on Structural and Magnetic Properties of $La_{0.5}Ca_{0.5}MnO_3$ Thin Films

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Received: 10 November 2008 / Accepted: 10 November 2008 / Published online: 25 November 2008

Abstract $La_{0.5}Ca_{0.5}MnO_3$ films with a nominal thickness of 80 nm were epitaxially grown on (001) $SrTiO_3$ and $SrLaAlO_4$ substrates by the pulsed laser deposition technique. The magnetic moment of the films was observed to depend strongly on the oxygen stoichiometry, tuned by heat treatments in vacuum and O_2 environments. A distinctly larger out-of-plane lattice parameter was measured for the vacuum-annealed films due to transformation of some Mn^{4+} ions to Mn^{3+}. Both the variations in the magnetic moment and out-of-plane lattice parameter during vacuum annealing can be recovered by subsequent heat treatments in O_2 environment. In this study, it is shown that the enhancement of the magnetic moment via O_2 annealing is considerably less prominent than the respective improvement obtained by the application of compressive epitaxial strain.

Keywords Manganites · Vacuum annealing · O_2 annealing · Thin film · Pulsed laser deposition

1 Introduction

Various studies have recently been devoted to electronic, magnetic and structural properties of $La_{(1-x)}Ca_xMnO_3$ due to its peculiar property called colossal magnetoresistance (CMR), defined as the extremely strong dependence of electrical resistivity on the applied magnetic field. This property makes $La_{(1-x)}Ca_xMnO_3$ a promising candidate for the device applications [1–6]. One step further, deposition of this material in the form of thin film provides new parameters such as epitaxial strain and film thickness to tune in order to reach the desired state [7–9].

Oxygen stoichiometry, which can be varied by heat treatments in vacuum and O_2 environments, has been shown to have a crucial role in determining the structural and electronic states of several oxide thin films [10–12]. The response of the oxide to the heat treatments mentioned above can be considerably different. For instance, the resistance of Sr_2FeMoO_6 films deposited on (100) $SrTiO_3$ (STO) substrate increases during O_2 annealing, explained by the formation of high resistance regions in grain boundaries, whereas $La_{0.67}Ca_{0.33}MnO_3$, in the ferromagnetic (FM) phase, deposited on (100) $NdGaO_3$ (NGO), becomes more metallic, conceivable recognizing the inverse relation between the hole concentration and the O vacancies [12]. It should be noted here that a great majority of the data reported for $La_{(1-x)}Ca_xMnO_3$ system are for the composition around $x = 0.3$ [10–12]. Consequently, the response of different compositions of this family to heat treatments in both vacuum and O_2 atmosphere is of particular interest to understand whether some additional mechanisms are at work for the compositions having other electronic phases (e.g. the charge-ordered antiferromagnetic (CO-AFM) phase) or not. Furthermore, data concerning the relative extent of O stoichiometry and epitaxial strain effects are lacking in literature.

In this study, 80-nm thick $La_{0.5}Ca_{0.5}MnO_3$ (LCMO) thin films, at the boundary between the CO-AFM and the FM phase fields are deposited on (001) STO and $SrLaAlO_4$ (SLAO) substrates. The resulting variations in the structural and magnetic properties due to heat treatments in vacuum and O_2 environments are presented and discussed in the light of the previously reported data about O stoichiometry in $La_{0.67}Ca_{0.33}MnO_3$. In addition, the deposition of the same

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film on above-mentioned two substrates allows the comparison of two parameters, namely, concentration of O vacancies and the epitaxial strain imposed by the substrate.

2 Experimental

The 80-nm thick LCMO films were deposited on (001) planar STO and SLAO substrates by pulsed laser deposition technique at 1073 K under oxygen pressure of 0.4 mbar and, subsequently, annealed at 1173 K for 30 minutes in ambient oxygen pressure.

Two kinds of post-annealing procedures were applied to the film on STO: (i) The films were annealed at 773 K in vacuum (pressure $\sim 10^{-5}$ mbar) for one hour, referred to vacuum annealing throughout the paper. (ii) Specimens were heated up to 1223 K and isothermally annealed at this temperature for one hour in a tube furnace with an O_2 flow of 7 mbar l/s, the so-called O_2 annealing.

X-ray diffraction (XRD) measurements were performed by a four-circle Bruker D8 Discover diffractometer, equipped with a Cu X-ray tube, Göbel mirror, 4-bounce 022 Ge channel-cut monochromator (to select only the Cu $K\alpha_1$ radiation), Eulerian cradle and a scintillation counter. The 002 reflection of the STO substrate was employed as a reference to identify the possible peak shifts during different the heat treatments.

The temperature dependence of magnetic moment was monitored by a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer in the range between 300 and 5 K. The magnetic field (0.01 T) was oriented parallel to the film surface.

3 Results and Discussion

The representative $2\theta - \omega$ scan (2θ is the angle between the incident and the diffracted X-ray beams; ω is the angle between the incident beam and the specimen surface) of the as-deposited films (see Fig. 1) shows that single phase and epitaxial LCMO thin films (the epitaxial quality of the films were confirmed by pole figure measurements; results not shown) were successfully grown on both kinds of substrates.

XRD patterns of the as-deposited, vacuum annealed (at 773 K) and, afterwards, O_2 annealed (at 1223 K) 80-nm LCMO films on (001) STO are seen in Fig. 2. It follows that the 040 reflection of the film shifts to lower 2θ values, representing an increase in the out-of-plane lattice parameter, during vacuum annealing. The expansion of the out-of-plane lattice parameter is presumably caused by the increase in the concentration of O vacancies since two Mn^{4+} ions should be converted to Mn^{3+}, which has a larger ionic size

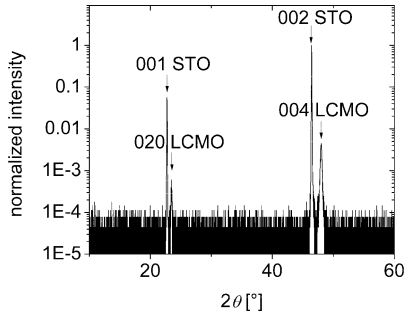

Fig. 1 The representative $2\theta - \omega$ scan of the as-deposited LCMO films

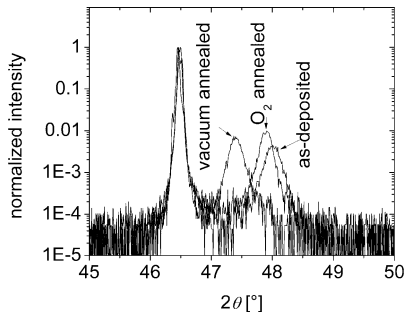

Fig. 2 The 040 reflection of the LCMO film deposited on STO in as-deposited condition, after vacuum annealing at 773 K for 1 h and after O_2 annealing at 1223 K for 1 h

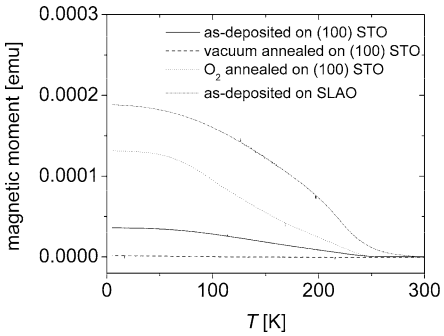

Fig. 3 The magnetic moment as a function of temperature for the LCMO film deposited on STO in the as-deposited condition, after vacuum annealing at 773 K for 1 h and after O_2 annealing at 1223 K for 1 h and for the LCMO film deposited on SLAO in the as-deposited condition

than the former, to satisfy the charge neutrality in the lattice. On the other hand, the 040 reflection of LCMO returns close to its initial position in the as-deposited condition after the O_2 annealing.

The magnetization measurements of the film in the as-deposited state and after heat treatments are presented in Fig. 3. It is clear that magnetic moment of the film is significantly reduced by vacuum annealing, whereas it can even exceed the values measured for the as-deposited film after a second heat treatment in O_2 environment. In addition, the Curie temperature decreases from 250 K (for the as-

deposited state) to approximately 140 K after vacuum annealing and, then, it is increased back to 240 K by subsequent O_2 annealing. It should be noted here that O_2 annealing at 773 K for one hour is not sufficient to recover the magnetic moment and, also, to shift the 040 reflection of LCMO peak back to its original position. This result can be explained by the slower kinetics of O-inward diffusion to the LCMO lattice than the outward diffusion from the film, in line with the data reported in [12]. A remarkable decrease in the amount of Mn^{4+} ions compared to the amount of Mn^{3+} ions may increase the Jahn–Teller distortion and, in addition, weaken the double-exchange interaction, leading to reduced magnetic moment and conductivity [13–15].

In addition, Fig. 3 provides information about the relative importance of two parameters, namely, O stoichiometry and epitaxial strain. It follows that the largest magnetic moment that can be achieved by O_2 annealing at temperatures as high as 1223 K is far surpassed by the as-deposited film on SLAO substrate. The compressive epitaxial strain imposed by SLAO can have two consequences: (i) The formation of the CO-AFM phase is hindered by the distortion caused by the in-plane contraction in the LCMO film. (ii) The compressive epitaxial stain can stabilize more O anions in the lattice, which in turn can increase the relative amount of Mn^{4+} ions.

4 Conclusion

As a conclusion, similar to the previously reported results for $La_{0.67}Ca_{0.33}MnO_3$, O stoichiometry has a strong effect on magnetic properties of $La_{0.5}Ca_{0.5}MnO_3$ thin films. Post-annealing treatment in vacuum is observed to decrease the magnetic moment of the film, whereas the original values are recovered after a subsequent O_2 annealing. The enhancement of the magnetic moment employing SLAO substrate is found to be distinctly larger than the maximum value reached by O annealing at temperature as high as 1223 K for one hour, highlighting the importance of strain parameter for manganites.

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